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| AB   | Low- or no VOC acrylic and vinyl copolymer latex, useful for coatings,<br>paints and inks, is prepared by using nonvolatile reactive amines as<br>neutralizers, (non)hydroxyl-containing unsatd. esters and/or ethers and/or<br>ether-esters and saturated hydroxyl-containing etherified and/or esterified<br>oligomeric glycols and/or oligools as coalescents, and hypersurfactants<br>replacing volatile amines and/or ammonia, organic solvents, and conventional<br>soaps and/or dispersants and/or detergents, resp. |          |                 |            |
| IT   | 228718-16-9<br>RL: NUU (Other use, unclassified); USES (Uses)<br>(coalescents; preparation of acrylic-based copolymer latex coatings with low<br>environmental toxicity)  |          |                 |            |
| RN   | 228718-16-9 CAPLUS  |          |                 |            |
| CN   | 1-Propanol, 3-[3-[3-(1-methylethoxy)propoxy]propoxy]- (9CI) (CA INDEX<br>NAME)  |          |                 |            |

i-PrO- (CH<sub>2</sub>)<sub>3</sub>-O- (CH<sub>2</sub>)<sub>3</sub>-O- (CH<sub>2</sub>)<sub>3</sub>-OH

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| <b>(54) Title:</b> LOW ENVIRONMENTAL TOXICITY LATEX COATINGS<br><br><b>(57) Abstract</b><br><br>Combinations of nonvolatile reactive amines, and hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters (and/or combinations of non-hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters, and saturated hydroxyl bearing etherified and/or esterified oligomeric glycols and/or oligools), as replacements for conventionally employed volatile amines and/or ammonia as neutralizers, and organic solvents as coalescents respectively, has been found to enable the production of economical, low to no VOC acrylic and vinyl copolymer latex based coatings, paints, and inks. Further enhancement may be had by substitution of hypersurfactants, in place of conventional soaps and/or dispersants and/or detergents, in combination with the aforementioned nonvolatile reactive amines, particularly as particulate dispersants in pigmented and/or reinforced coatings. |           |   |

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## LOW ENVIRONMENTAL TOXICITY LATEX COATINGS

1 Background of The Invention:

2       The use of ammonia and/or volatile amines as neutralizing  
3 agents and/or stabilizers, and of alcohols, glycols, and glycol  
4 monoethers and monoesters, often in combination, at levels to 40%  
5 by volume (exclusive of water) has been employed for more than  
6 fifty years to achieve the coalescence of latex solids in acrylic,  
7 polyvinyl acetate and related copolymer resins based coatings.  
8 The volatilization of these conventional neutralizers, and  
9 coalescing components, after achieving film coalescence is  
10 normally required in order to inhibit the resultant film's  
11 breakdown (reversion) in the presence of humid environments, and  
12 to provide acceptable wear and stain resistance to the dried film.

13       Recent concerns regarding the environmental degradation  
14 (predominantly low level ozone formation), and the health and fire  
15 hazards associated with exposure to ammonia, volatile amines and  
16 volatile organics (VOCs), has led to increasingly strict  
17 regulatory limitations on the nature, and proportions, of VOCs  
18 which may be employed in coatings. One technique that has been  
19 employed in order to comply with said limitations in latex coating  
20 applications is the development of self coalescing latex resins  
21 which require no coalescents. However, to date, such materials  
22 have had the disadvantage of being limited to low Tg film formers  
23 with poor performance properties.

24 Subject of The Invention:

25       This invention teaches the use of low levels of combinations  
26 of nonvolatile reactive amines, in combination with hydroxyl

1 bearing unsaturated esters and/or ethers and/or ether-esters,  
2 and/or non-hydroxyl bearing unsaturated esters and/or ethers  
3 and/or ether-esters and incompletely etherified and/or esterified  
4 oligomeric glycols and/or oligools as partial or full replacements  
5 for conventionally employed volatile amines and/or ammonia as  
6 neutralizers, and organic solvents as coalescents, respectively,  
7 in latex resin applications. This invention has the advantage of  
8 reducing emissions and enhancing the performance of films produced  
9 from conventional latex resins, and when employed in conjunction  
10 with certain types of hypersurfactants (cf. Table 5) also  
11 upgrades pigment and/or extender dispersion, and reduces grind  
12 times in particulate containing variants; thus enhancing plant and  
13 energy use efficiencies. Synergistic performance enhancement, and  
14 VOC reduction in latex resins may be attained via the employment  
15 of the aforementioned technologies in combination. Partial  
16 replacement of either or of both of the aforementioned components  
17 by the alternatives of this invention is shown to provide lesser,  
18 but still desirable benefits.

19 Preferred Embodiment of The Invention

20       The non-volatile reactive amines useful in the practice of  
21 this invention have vapor pressures below 0.1 mm Hg at 25°C,  
22 contain at least one basic nitrogen, and at least one carbon to  
23 carbon double bond, and/or a transition metal ligand, and contain  
24 no more than twelve carbon atoms per basic nitrogen atom. Those  
25 more preferable contain one or more (meth)acryl and/or N-vinyl  
26 ligands, and those most preferable have a water solubility

1 exceeding 2% at 25°C. Specific examples of such useful non-  
2 volatile reactive amines are given in Table (1). These examples  
3 are intended to be illustrative rather than exhaustive of the  
4 scope of useful materials.

5  
6 TABLE I

|    |      |   |
|----|------|---|
| 7  | (1A) | N-vinyl pyrrolidone                                       |
| 8  | (1B) | N,N,N'-tris (2-butenyl), ethylene diamine                 |
| 9  | (1C) | N', methyl-1, 3-propylene diamine mono 2- propenamide     |
| 10 | (1D) | N, 2-propenyl, bis (2-hydroxy)propyl amine                |
| 11 | (1E) | N, 2-propenyl, N'- (2-hydroxy)ethyl, hexamethylene        |
| 12 |      | triamine  |
| 13 | (1F) | 4-(N, 3-hydroxypropyl, N-vinyl) 2-amino ethyl 2-butenate  |
| 14 | (1G) | 2-[N,-(2-oxa-cyclopentadienyl)] amino acetic acid ethyl   |
| 15 |      | ester   |
| 16 | (1H) | 4-(N,N bis vinyl) 1,3-pentanediol                         |
| 17 | (1I) | tetraethylene glycol mono 3-( N, ethyl) amino, 2-(methyl) |
| 18 |      | 2-propenoate  |
| 19 | (1J) | N,N-divinyl glutamic acid 2-propenyl ester                |
| 20 | (1K) | 6-(N,N bis vinyl) hexanoic acid ethyl ester               |
| 21 | (1L) | Titanium IV tetrakis N, 2-aminoethyl ethanolato           |

22 The preferred types of the hydroxyl bearing, unsaturated  
23 esters and/or ethers and/or ether-esters useful in the practice  
24 of this invention are those having vapor pressures below 0.1 mm  
25 Hg at 25°C, which are capable of air initiated, oxidative  
26 oligomerization and/or polymerization derived non-reversible

1 bonding, under normal latex application conditions, to film  
2 component(s) and/or to substrate, in order to maximize coating  
3 properties via crosslinking the resulting latex thereby  
4 minimizing its (post film formation) environmental sensitivity.  
5 Examples of such unsaturated esters and ether and ether-esters as  
6 are useful in the practice of the instant invention are provided  
7 in Table II. These examples are intended to be illustrative  
8 rather than exhaustive of the scope of useful materials.

9 Table II

- 10 (2A) trimethylol propane bis (2-methyl)-2-propenoate ester  
11 (2B) sorbitan tetrakis 2-butenate ester  
12 (2C) bis pentaerythritol 2-propenolate, tris 2-propenoate ester  
13 (2D) hexanoic acid 6-hydroxy, (2-propenoate)ethyl ester  
14 (2E) citric acid mono isodecenyl ester  
15 (2F) malic acid bis cinnamyl ester  
16 (2G) 3-heptanoyl furfuryl alcohol  
17 (2H) 1,2,3-propanetriol 1-vinyl ether, 2-phenyl carboxylate ester  
18 (2J) trimeric 2-butenediol mono (methyl) glutarate ester  
19 (2K) ethoxylated (4) bis phenol A mono 2-propenoate ester

20 The preferred types of the non-hydroxyl bearing unsaturated  
21 esters and/or ethers and/or ether-esters useful in conjunction with  
22 the practice of this invention are those having vapor pressures  
23 below 0.1 mm Hg at 25°C, which are capable of air initiated  
24 oxidative oligomerization and/or polymerization, and non-reversible  
25 bonding, under normal latex application conditions, to film  
26 component(s) and/or to substrate, in order to maximize coating

1 properties via crosslinking the resulting latex thereby minimizing  
2 its (post film formation) environmental sensitivity. Examples of  
3 such non- hydroxyl bearing unsaturated esters and ether and ether-  
4 esters as are useful in the practice of the instant invention are  
5 provided in Table III. These examples are intended to be  
6 illustrative rather than exhaustive of the scope of useful  
7 materials.

8 Table III

- 9 (3A) trimethylol propane bis (2-methyl)-2-propenoate ester, mono  
10 vinyl ether  
11 (3B) 1,2,3-propane triol tris 2-butenate ester  
12 (3C) penta erythritol 2-propenolato, tris 2-propenoate ester  
13 (3D) hexanoic acid 6-acetoxy, (2-propenoato)ethyl ester  
14 (3E) fumaric acid bis isodecyl ester  
15 (3F) maleic acid bis cinnamyl ester  
16 (3G) furoic acid vinyl ester  
17 (3H) 1,2,3-hexanetriol 1,2-bis vinyl ether, phenyl carboxylate  
18 ester  
19 (3J) trimeric 2-butene-1,4-diol bis propionate ester  
20 (3K) ethoxylated (4) bisphenol A bis 2-(methyl)-2-propenoate ester

21 The preferred types of the incompletely etherified and/or  
22 esterified oligomeric glycols and/or oligools useful in the  
23 practice of this invention are those having vapor pressures below  
24 0.1 mm Hg at 25°C, which are oligomers of two to 4 carbon diols,  
25 and of three to six carbon triols, wherein each of the ether and/or  
26 ester ligands contains five or fewer carbon atoms per oxygen.



1 Examples of such incompletely etherified and/or esterified  
2 oligomeric glycols and/or oligoals as are useful in the practice of  
3 the instant invention are provided in Table IV. These examples are  
4 intended to be illustrative rather than exhaustive of the scope of  
5 useful materials.

6 Table IV

- 7 (4A) penta (ethylene glycol) mono methyl ether  
8 (4B) tetra (1,4-butylene glycol) mono (2-methyl) butyrate  
9 (4C) 1-hydroxy-2,5-bis methyl-3,6,9,12-tetraoxa tetradecane  
10 (4D) 4-oxaheptane-1,2,6,7-tetraol mono acetate, mono 2-propyl  
11 ether (mixed isomers)  
12 (4E) ethoxylated (6) 1,2,4-butanetriol bispropanoate (mixed  
13 isomers)  
14 (4F) tris 1,2,5-n pentane triol tetraethyl ether (mixed isomers)  
15 (4G) tris (1,3-propane-diol) mono isopentyl ether  
16 (4H) 1,2- bis (2- hydroxy ethoxy ethyl) 1,2,3-propane triol  
17 (4J) polyethylene glycol (300) mono amyl ether  
18 (4K) tris neopentyl glycol mono n-propyl ether

19 The surfactants most useful in the practice of this invention  
20 are those having vapor pressures below 0.1 mm Hg at 25°C, which are  
21 capable of non-reversible bonding, under normal processing  
22 conditions, to film component(s) and/or substrate in order to  
23 maximize coating properties, while minimizing post film formation  
24 environmental sensitivity, and which serve to efficiently wet  
25 substrates coated, and to disperse particulates, if any, employed  
26 in the formulated latex coating. Among the surfactants found to be

1 useful in the practice of this invention are amphoteric detergents,  
2 and certain organometalics based on tetravalent titanium or  
3 zirconium. These last have been found to contribute significantly  
4 to substrate adhesion and improved corrosion resistance on wood,  
5 metallic and ceramic substrates, and to be particularly useful in  
6 maximizing color intensities of carbon black, azo and  
7 phthalocyanine based pigments. Specific examples of the preferred  
8 types of hypersurfactants are given in Table V. These examples are  
9 intended to be illustrative rather than exhaustive of the scope of  
10 useful materials.

11 Table V

- 12 (5A) 12-N,N,N-trimethylaminododecanoato  
13 (5B) N-(pentakis oxyethylene sulfato) triethylene diamine  
14 (5C) p-[6-N(methyl) morpholino]octyl phenyl phosphonic acid  
15 (5D) N,N,N-triethyl glutamic acid  
16 (5E) titanium 4 octyl, [(tris octyl) diphosphato  
17 (5F) titanium 4 oxoethylene, bis (dodecyl) phenylsulfonato  
18 (5G) oxy [bis titanium 4 (bis tridecyl) diphosphate]  
19 (5H) zirconium 4 tetraethylene glycol monomethyl ether, tris  
20 (tetraethylene glycol monomethyl ether) diphosphato  
21 (5J) zirconium 4, bis w-N,N-(dimethyl)amino octanoato, 1,4-  
22 cyclohexanediolato  
23 (5K) triethylene glycol diolato, bis [zirconium 4 tris (octyl)  
24 phosphate]

25 Those skilled in the art shall no doubt be capable of  
26 subverting the teachings of this invention via the substitution of

1 functionally equivalent materials, e.g. employment in combination  
2 of hydroxylated and non-hydroxyl bearing esters (ether-esters)  
3 optionally in combination with partially esterified and/or  
4 etherified glycols, and or polyols, in place of either component  
5 (set) alone, (as is amply demonstrated in example No. 4.), or of  
6 unsaturated analogous unsaturated amides, for a portion of the  
7 aforementioned unsaturated ethers, esters or ether-esters disclosed  
8 above, and/or fluorination of one or more of the species of  
9 components heretofore described as necessary to the successful  
10 practice of this invention; however such non-critical  
11 modifications, and/or combinations of relevant species types, must  
12 be considered as within the scope of this disclosure.

13 Further amplification of the scope and utility of the instant  
14 invention to latex coating applications in inks, paints and stains  
15 shall be found to be illustrated by the content(s) of examples 1  
16 through 5. Said examples are intended to be illustrative rather  
17 than exhaustive of the extraordinarily diverse applicability of the  
18 instant invention.

19 Example #1

20 This example teaches the superiority of the present invention  
21 versus the prior art with respect to the productivity, VOC  
22 emissions, and performance quality in a masonry sealer application.

23 A masonry sealer formulation was prepared by the sequential  
24 dispersion of the indicated components (pigment dispersion times  
25 and grind quality achievement was noted). The resulting sealer was  
26 applied via roller to smooth surface, ten day old, 8" X 18" X 1"

1 thick concrete castings, at an application rate of one gallon per  
 2 400 square foot, dry time (to touch) was measured under conditions  
 3 of 72° F and 85% humidity. After 240 hours of drying @ 72° F and  
 4 85% humidity, sealer performance was measured by weighing the dry  
 5 casting, then impounding a 6" depth of water, or alternatively 6%  
 6 salt solution, on such a casting for twenty four hours, then  
 7 draining and weighing the drained casting. The weight percent of  
 8 water, and independently that of 6% salt solution, adsorbed by said  
 9 castings were used to determine sealer efficacy. The results of  
 10 this study are given in Table No. 1.

11 **Formulation:** in parts by weight; (in order of addition) water  
 12 200.0; neutralizer<sup>1</sup>, as shown; surfactant<sup>a</sup>, as shown, biocides<sup>2</sup>,  
 13 18.50; hydroxy ethyl cellulose, 5.00; potassium tris polyphosphate,  
 14 2.00; defoamer<sup>2</sup>, 1.00; coalescent<sup>a</sup>, as shown; ultramarine blue  
 15 pigment, 0.25; rutile titanium dioxide, 200.0, American process  
 16 zinc oxide, 25; platey talc, 250; water, 49.98; AC-625 Acrylic  
 17 latex resin<sup>3</sup>, 352.0; defoamer<sup>2</sup>, 0.98; surfactant<sup>b</sup>, coalescent<sup>b</sup>, as  
 18 shown,; water, 24.99; and sodium nitrite 2.30; thixotrope<sup>4</sup>, as  
 19 shown (required) to adjust system viscosity to 85-90 KU at 75° F.

20 Table No. 1

| 21 | <u>Formulation</u> | <u>1</u>                       | <u>2</u> | <u>3</u> | <u>4</u> | <u>5</u> |
|----|--------------------|--------------------------------|----------|----------|----------|----------|
| 22 | neutralizer        | amp-95/1.98                    | 1B/2.00  | 1H/1.80  | 1G/2.20  | 1D/1.78  |
| 23 | surfactant(a)      | Tamol 850 <sup>7</sup> /14.85  | 5A/1.80  | 5E/1.75  | 5K/1.55  | 5H/1.50  |
| 24 | coalescent(a)      | Propylene glycol               | none     | none     | 4J/4.50  | none     |
| 25 |                    | /34.56                         |          |          |          |          |
| 26 | surfactant(b)      | Triton N101 <sup>3</sup> /2.20 | none     | 5B/1.00  | none     | 5D/1.25  |
| 27 | coalescent(b)      | Texanol <sup>8</sup> /9.88     | 2A/16.42 | 3A/12.60 | 3F/18.55 | 2H/11.70 |
| 28 |                    |                                |          |          |          |          |

| <u>Formulation</u> | <u>6</u>                       | <u>7</u>                | <u>8</u>               | <u>9</u> | <u>10</u>                 |
|--------------------|--------------------------------|-------------------------|------------------------|----------|---------------------------|
| neutralizer        | ammonia/1.00<br>1L/1.00        | 1B/1.00<br>ammonia/1.00 | 1H/1.80<br>AMP-95/1.00 | 1G/1.20  | 1D/1.78                   |
| surfactant (a)     | Tamol 850 <sup>7</sup> /14.85  | 5A/1.80                 | 5E/0.75                | 5K/1.55  | 5H/0.75                   |
| surfactant (b)     | Triton N101 <sup>6</sup> /2.20 | none                    | Triton N101<br>/2.20   | none     | 5D/1.25                   |
| coalescent (a)     | Propylene glycol<br>/34.56     | none                    | none                   | 4J/4.50  | Propylene glyco<br>/17.88 |
| coalescent (b)     | Texanol <sup>8</sup> 19.98     | 2A/16.42                | 3A/12.60               | 3F/18.55 | 2H/5.85                   |

| <u>Formulation</u> | <u>VOC g/l<sup>5</sup></u> | <u>Dispersion<br/>time hr.</u> | <u>Grind<br/>Hegman</u> | <u>Water<br/>adsorption g.</u> | <u>Salt water<br/>adsorption g.</u> |
|--------------------|----------------------------|--------------------------------|-------------------------|--------------------------------|-------------------------------------|
| 1                  | 124                        | 3.4                            | 4                       | 46                             | 61                                  |
| 2                  | 8                          | 0.7                            | 6                       | 27                             | 32                                  |
| 3                  | 3                          | 0.6                            | 6                       | 21                             | 28                                  |
| 4                  | 5                          | 0.7                            | 5                       | 24                             | 27                                  |
| 5                  | 4                          | 0.6                            | 6                       | 25                             | 30                                  |
| 6                  | 112                        | 3.1                            | 4                       | 37                             | 48                                  |
| 7                  | 10                         | 0.7                            | 6                       | 32                             | 42                                  |
| 8                  | 3                          | 2.4                            | 5                       | 27                             | 38                                  |
| 9                  | 6                          | 0.7                            | 5                       | 24                             | 27                                  |
| 10                 | 36                         | 1.8                            | 6                       | 31                             | 39                                  |

Notes: a) As shown; 1) A combination of 3.5 parts of Nuosept 95, and 15 parts of Nuocide 404D, Huls Corp. were employed; 2) Defo 806-102; Ultra Inc. 3) AC-625, Union Carbide Corp.; 4) Rhevis CR, Rhevis Corp. 5) via EPA Method 24GC; 6) Rohm and Haas Corp.; 7) Eastman Kodak Inc.

The efficacy of the coalescent systems of the instant art in producing a less water and salt permeable, acrylic latex based masonry seal coating, is compared to a conventionally coalesced counterpart, Formulation No. 1, and is obvious from the preceding data. VOC emissions reduction and improvement in both productivity and dispersion level achieved are likewise self evident.

#### Example #2

This example teaches the superiority of the present invention versus the prior art with respect to the productivity, VOC

1 emissions, and performance quality in a direct to metal,  
2 maintenance coating application.

3 Direct to metal coatings were prepared by the sequential  
4 dispersion of the indicated components (pigment dispersion times  
5 were noted). The resulting coating was spray applied to sandblasted  
6 smooth surface 24" X 8" carbon steel test panels at application  
7 rate of one gallon per 250 square feet. After 120 hours of drying  
8 @ 72° F and 85% humidity, edge sealing and scribing, the coatings'  
9 corrosion resistance performance were each measured by QUV cabinet  
10 exposure [cyclic exposure to UV radiation, 4% saline solution, and  
11 varying temperature (25°-80° C)].

12 **Formulation:** in parts by weight (in order of addition): water,  
13 50.0; neutralizer, as shown; Surfactant<sup>a</sup>, as shown, biocide<sup>1</sup>, 4.00;  
14 oxidized polyethylene wax, 4.00; (disperse wax) polyurethane  
15 thixotrope<sup>2</sup>, as shown; defoamer<sup>3</sup>, 2.00; coalescent<sup>a</sup>, as shown,  
16 ultramarine blue pigment, 0.25; rutile titanium dioxide, 125; zinc  
17 aluminate 150; Acrylic latex resin<sup>4</sup>, 64.0; (disperse particulates  
18 to Hegman 7.5+). Neutralizer, is shown; acrylic latex resin<sup>4</sup>,  
19 564.0; defoamer<sup>2</sup>, 0.98; surfactant<sup>b</sup>, coalescent<sup>b</sup>, as shown; water,  
20 16.00; arid sodium nitrate 2.30. Thixotrope<sup>2</sup>, (as required) to  
21 adjust system viscosity to 80-85 KU at 75° F . The control coating  
22 required 3.7 hours to disperse to a Hegman grind gauge reading of  
23 7+, whereas each of the instant art coatings achieved said fineness  
24 of grind in less than one half hour. The results of this study are  
25 given in Table No. 2

26

Table No. 2

| <u>Formulation</u>      | <u>1</u>                        | <u>2</u>                 | <u>3</u>          | <u>4</u>                      | <u>5</u>  | <u>6</u>                                |
|-------------------------|---------------------------------|--------------------------|-------------------|-------------------------------|-----------|---|
| neutralizer             | DMAMP-80 <sup>5</sup> /12.5     | 1A/4.00                  | 1C/1.80           | 1E/2.20                       | 1J/1.78   | DMAMP-80 <sup>5</sup> /6.25<br>1A/ 2.00 |
| surfactant (a)          | Triton CF10 <sup>6</sup> /10.00 | 5D/1.80                  | 5F/1.75           | 5C/1.55                       | 5J/1.50   | Triton CF 10/5.00                       |
| thixotrope <sup>2</sup> | 15.00                           | 5.00                     | 5.50              | 8.70                          | 5.30      | 9.32                                    |
| coalescent (a)          | Diproylene glycol /34.60        | 4B/12.00                 | 4E/10.5           | 4K/8.25                       | none      | none                                    |
| surfactant (b)          | none                            | none                     | 5A/1.00           | Triton CF10 <sup>6</sup> .4.0 | none      | 5D/1.25                                 |
| coalescent (b)          | PmPE <sup>7</sup> /44.60        | 2A/16.42                 | 3A/12.60          | 3F/18.55                      | 2H/14.70  | 2H/14.70                                |
| thixotrope <sup>2</sup> | 21.40                           | 4A/7.45<br>3.20          | 1.50              | 0.70                          | 2.30      | 1.95                                    |
| <u>Formulation</u>      | <u>7</u>                        | <u>8</u>                 | <u>9</u>          | <u>10</u>                     | <u>11</u> | <u>12</u>                               |
| neutralizer             | DMAMP-80 <sup>5</sup> /12.5     | 1A/4.00                  | 1C/1.80           | 1E/2.20                       | 1J/1.78   | DMAMP 80 <sup>5</sup> /6.25             |
| surfactant (a)          | Triton CF10 <sup>6</sup> /10.00 | 5D/1.80                  | 5F/1.75           | 5C/0.55                       | 5J/1.50   | Triton CF10/5.00                        |
| surfactant (b)          | none                            | none                     | 5A/1.00           | Triton CF10 <sup>6</sup> /2.0 | none      | 5D/1.25                                 |
| thixotrope <sup>2</sup> | 15.00                           | 5.00                     | 5.50              | 8.70                          | 5.30      | 9.32                                    |
| coalescent (a)          | Dipropylene glycol /17.3        | PmPE <sup>7</sup> /22.60 | 4B/12.00          | 4E/10.5                       | 4K/8.25   | PmPE <sup>7</sup> /22.3                 |
| coalescent (b)          | 2A/ 8.81                        | 2A/ 6.42                 | PmPE <sup>7</sup> | 3F/ 18.55<br>4A/7.45          | 2H/14.70  | 2H/14.70                                |
| thixotrope <sup>2</sup> | 18.90                           | 6.20                     | 4.50              | 3.70                          | 2.30      | 6.95                                    |

| <u>Formulation</u> | <u>VOC g/l<sup>8</sup></u> | <u>Initial gloss</u> | <u>60° gloss @</u> | <u>60° gloss @</u>  | <u>60° gloss @</u>   |
|--------------------|----------------------------|----------------------|--------------------|---------------------|----------------------|
|                    |                            | <u>@60°</u>          | <u>200hr. QUV</u>  | <u>500 hr. QUV.</u> | <u>1,000 hr. QUV</u> |
| 1                  | 232                        | 82                   | 76                 | 31                  | film destroyed       |
| 2                  | 9                          | 91                   | 87                 | 82                  | 76                   |
| 3                  | 11                         | 93                   | 90                 | 88                  | 80                   |
| 4                  | 8                          | 87                   | 86                 | 82                  | 61                   |
| 5                  | 10                         | 88                   | 86                 | 85                  | 84                   |
| 6                  | 13                         | 84                   | 80                 | 66                  | 59                   |
| 7                  | 72                         | 85                   | 79                 | 46                  | 12                   |
| 8                  | 57                         | 80                   | 76                 | 51                  | 18                   |
| 9                  | 28                         | 87                   | 84                 | 72                  | 63                   |
| 10                 | 7                          | 88                   | 86                 | 84                  | 78                   |
| 11                 | 8                          | 92                   | 90                 | 87                  | 85                   |
| 12                 | 77                         | 85                   | 80                 | 75                  | 48                   |

Notes: 1) Nuosept 95, -Huls Corp. 2) Acrysol RM 2020, Rohm and Haas 3) Defo 3000; Ultra Inc. 4) HG 56, Rohm and Haas Corp. 5) 80%

1 2-N,N-dimethylamino-2-methyl propanol aq. 6) Union Carbide Corp. 7)  
2 propylene glycol mono phenyl ether. 8) via EPA Method 24GC

3 The efficacy of the coalescent systems of the instant art in  
4 producing a more environmentally resistant, acrylic latex based  
5 direct to metal coating, as compared to a conventionally coalesced  
6 counterpart, Formulation No. 1, is obvious from the preceding data.  
7 VOC emissions reduction, and improvement in productivity achieved  
8 are likewise self evident.

9 Example #3

10 This example teaches the superiority of the present invention  
11 versus the prior art with respect to productivity, VOC emissions,  
12 and performance quality in a polyvinyl acetate based interior flat  
13 architectural paint application.

14 Interior flat paints, were prepared by the sequential  
15 dispersion of the indicated components (pigment dispersion times,  
16 and dispersion efficacy were noted). The resulting coating was  
17 brush applied to unprimed drywall (gypsum sheet) @ 72° F and 80%  
18 humidity, coverage, stain removal, and scrubability performance  
19 were each measured after 7 days of drying 72+/- 2° F @ 65-80%  
20 humidity.

21 Formulation; in parts by weight; (in order of addition) water,  
22 200.0; neutralizer<sup>1</sup>, as shown; surfactant<sup>a</sup>, as shown, biocides<sup>2</sup>,  
23 1.00; hydroxy ethyl cellulose, as shown; potassium tris  
24 polyphosphate, as shown; defoamer<sup>3</sup>, 1.00; coalescent<sup>a</sup>, as shown;  
25 ultramarine blue pigment, 0.25; rutile titanium dioxide, 250.0,  
26 water washed clay<sup>4</sup>, 50.0; calcium carbonate<sup>5</sup>, as shown; diatomite<sup>6</sup>,



1 50.0; water, 49.98; PVA latex resin<sup>7</sup>, 352.0; defoamer<sup>2</sup>, 0.98;  
 2 coalescent<sup>b</sup>, as shown ; water, 100 .0;and sodium nitrite 2.30;  
 3 thixotrope<sup>8</sup>, as shown (required) to adjust system viscosity to 90-  
 4 100 KU at 75° F.

5 The results of this evaluation are shown in Table No. 3.

6 Table No. 3

| 7  | Formulation             | 1                 | 2              | 3                | 4               | 5        | 6           |
|----|-------------------------|-------------------|----------------|------------------|-----------------|----------|-------------|
| 8  | neutralizer             | 28% ammonia aq.   | 1B/2.00        | 1H/1.80          | 1G/2.20         | 1D/1.78  | 28% ammonia |
| 9  |                         | 6.05              |                |                  |                 |          | 6.05        |
| 10 | HEC(QP-4400)            | 5.50              | 1.20           | 1.35             | 1.25            | 1.40     | 1.35        |
| 11 | surfactant(a)           | Tamol 731/6.90    | 5E/1.80        | 5J/1.75          | 5C/1.55         | 5F/1.5   | Tamol 731/6 |
| 12 |                         | Triton N101/3.31  |                |                  |                 |          | Triton      |
| 13 |                         |                   |                |                  |                 |          | N101/3.31   |
| 14 | coalescent(a)           | Propylene glycol  | 4A/6.00        | 4 F/7.00         | 4H/5.50         | 4E/7.00  | 4E/7.00     |
| 15 |                         | /51.95            |                |                  |                 |          |             |
| 16 |                         | Texanol/9.88      |                |                  |                 |          |             |
| 17 | Calcite                 | 50                | 150            | 125              | 150             | 140      | 50          |
| 18 | coalescent(b)           | none              | 2A/26.4        | 3C/12.60         | 3F/18.50        | 2J/11.90 | 2J/11.90    |
| 19 | thixotrope <sup>8</sup> | 3.5               | 3.0            | 3.1              | 2.7             | 2.4      | 3.9         |
| 20 |                         |                   |                |                  |                 |          |             |
| 21 | Formulation             | 7                 | 8              | 9                | 10              |          |             |
| 22 | neutralizer             | 28% ammonia aq.   | 1B/2.00        | 1H/1.80          | 1H/1.80         |          |             |
| 23 |                         | 6.05              |                |                  |                 |          |             |
| 24 | HEC (QP-4400)           | 5.50              | 1.20           | 1.35             | 1.25            |          |             |
| 25 | surfactant(s)           | Tamol 731/ 6.9    | Tamol 731/ 3.9 | 5J/ 1.75         | Tamol 731/ 6.9  |          |             |
| 26 |                         | Triton N101/ 3.31 | 5J/1.0         |                  | Triton N101/ 3. |          |             |
| 27 | coalescent (a)          | Propylene glycol  | 4A/6.00        | Propylene glycol | 4H/5.50         |          |             |
| 28 |                         | 51.95             |                | 51.95            |                 |          |             |
| 29 | calcite                 | 50                | 100            | 125              | 150             |          |             |
| 30 | coalescent (b)          | 4E/2.00           | 2A/ 26.4       | 3C/ 12.60        | 3F/ 18.50       |          |             |
| 31 | thixotrope <sup>8</sup> | 3.5               | 3.0            | 3.1              | 2.7             |          |             |
| 32 |                         |                   |                |                  |                 |          |             |

| 34 | Formulation | VOC g/l <sup>9</sup><br>hr. | Dispersion Time | Grind<br>Hegman | Min.Coalescence<br>temp °C | Scrubs <sup>10</sup> | Stain Removal <sup>11</sup> |
|----|-------------|-----------------------------|-----------------|-----------------|----------------------------|----------------------|-----------------------------|
| 37 | 1           | 199                         | 2.4             | 4               | 47                         | 410                  | 6                           |
| 38 | 2           | 8                           | 0.4             | 5               | 34                         | 1,740                | 9                           |
| 39 | 3           | 3                           | 0.6             | 6               | 32                         | 2,025                | 10                          |
| 40 | 4           | 5                           | 0.6             | 6               | 36                         | 1,960                | 9                           |
| 41 | 5           | 4                           | 0.5             | 5               | 30                         | 2,230                | 10                          |
| 42 | 6           | 15                          | 2.2             | 4               | 31                         | 785                  | 8                           |
| 43 | 7           | 190                         | 2.4             | 4               | 43                         | 850                  | 7                           |
| 44 | 8           | 9                           | 0.9             | 5               | 35                         | 1,140                | 8                           |
| 45 | 9           | 188                         | 1.1             | 5               | 45                         | 890                  | 7                           |
| 46 | 10          | 8                           | 2.4             | 4               | 37                         | 1,310                | 8                           |

47  
 48 Notes: 1) As shown; 2) Nuosept 95, Huls Corp.; 3) Defo 3000; Ultra  
 49 Inc.. 4) 70C Huber Corp.5) Camel Carb., Cambel Corp.; 6) Diafil 530

viscosity of 65-70 KU, and the coating was applied by curtain coating on sanded but unprimed 4' X 8' X 0.25" laminate natural oak (on pine) substrate. The coated panels were force dried by passing same through a 180° F oven for 20 minutes, then cooled at ambient temperature (ca. 80° F) for 24 hours prior to evaluation, for abrasion and solvent resistance. to determine coating performance, efficacy. The results of this study are given in Table No. 4.

Table No. 4

| Formulation                | 1   | 2                                   | 3                                  | 4                                | 5            | 6    | 7    | 8    |
|----------------------------|---|-------------------------------------|------------------------------------|----------------------------------|--------------|------|------|------|
| <u>Part A:</u>             |   |                                     |                                    |                                  |              |      |      |      |
| neutralizer                | 28%   | 1A                                  | 1H                                 | 1H                               | 1H           | 1B   | 1B   | 1B   |
|                            | ammonia aq.                                     |                                     |                                    |                                  |              |      |      |      |
| <u>Part B: formulation</u> |   |                                     |                                    |                                  |              |      |      |      |
| Texanol                    | 8.00  |                                     |                                    |                                  |              |      | 4.00 | 4.00 |
| diethylene glycol          | 18.20   |                                     |                                    |                                  |              |      | 9.10 | 9.10 |
| mono butyl ether           |   |                                     |                                    |                                  |              |      |      |      |
| 2A                         |   | 12.05                               | 6.00                               |                                  | 6.00         | 6.00 | 6.00 |      |
| 2C                         |   |                                     | 4.40                               | 10.70                            |              |      |      |      |
| 3B                         |   |                                     |                                    |                                  | 4.20         |      |      | 6.00 |
| 4G                         |   |                                     | 1.90                               | 2.90                             | 1.05         | 6.20 |      |      |
| 4J                         |   |                                     |                                    |                                  |              |      |      |      |
| Formulation                | VOC g/l <sup>1</sup><br>resistance <sup>2</sup> | Abrasion<br>resistance <sup>3</sup> | Solvent<br>resistance <sup>4</sup> | Stain<br>hr. @ 80°F <sup>5</sup> | Mix pot life |      |      |      |
| 1                          | 165   | 114                                 | lifts                              | poor                             | 7.5          |      |      |      |
| 2                          | 3   | 31                                  | slight softening                   | good                             | 42           |      |      |      |
| 3                          | 4   | 29                                  | slight softening                   | fair                             | 35           |      |      |      |
| 4                          | 3   | 24                                  | no change                          | excellent                        | 40           |      |      |      |
| 5                          | 3   | 26                                  | no change                          | good                             | 61           |      |      |      |
| 6                          | 4   | 98                                  | mod. Softening                     | fair                             | 46           |      |      |      |
| 7                          | 83  | 19                                  | slight softening                   | fair                             | 21           |      |      |      |
| 8                          | 85  | 78                                  | severe softening                   | poor                             | 11           |      |      |      |

Notes: 1) By EPA Method 24GC; (formulations 2 through 7 produced 0 to negative VOC readings by EPA Methods 24, and 24A; 2) Tabor CS-10 wheel 1000 cycles; 3) 24 hr methyl ethyl ketone covered spot test; 4) 24 hr exposure to lipstick; 5) time to 10% loss of abrasion resistance in finished coating.

This example demonstrates, that the use of the combination of components cited as the basis of the instant invention, viz. That

1 Whittaker, Clark, and Daniels Inc. 7) Rhoplex 3077, Rohm and Haas  
2 Corp.; 8) Rhevis CR, Rhevis Corp. 9) via EPA Method 24GC. 10) ASTM  
3 method; 11) ASTM method.

4 The efficacy of the coalescent systems of the instant art in  
5 producing a more, scrub and stain resistant PVA latex based  
6 interior flat architectural coating as compared to a conventionally  
7 coalesced counterpart, Formulation No. 1, is obvious from the  
8 preceding data. VOC emissions reduction and improvement in both  
9 productivity and dispersion level achieved are likewise self  
10 evident, as is a considerable reduction in minimum coalescence  
11 temperature, without recourse to the use of low boiling, flammable  
12 solvent(s), normally employed to induce same.

13 Example #4

14 This example teaches the superiority of the present invention  
15 versus the prior art with respect to the productivity, VOC  
16 emissions, and performance quality in a force dried, clear,  
17 protective, two component acrylic latex cured - waterborne epoxy,  
18 wood cabinet coating.

19 Component A. neutralizing agent, as shown-3.5 PBW; sodium  
20 nitrite 0.15 and defoamer (Patcote 519-Patco Coatings Inc.) were  
21 admixed with 95.85 PBW of (Acrylic latex-Maincote AE 58), and said  
22 emulsion was subsequently mixed with 50 PBW of Component B,  
23 formulated by blending various additives, as shown, into 12.5 PBW  
24 of Genepoxy 370-H55- Daubert Chemical Co., and diluting as  
25 necessary with water to produce a total part B weight of 25 parts.  
26 Thixatropel, was added, as required, to provide an initial mix

1 nonvolatile reactive amines, in combination with hydroxyl bearing  
2 unsaturated esters and/or ethers and/or ether-esters, and/or non-  
3 hydroxyl bearing unsaturated esters and/or ethers and/or ether-  
4 esters and incompletely etherified and/or esterified oligomeric  
5 glycols and/or oligools as (partial or full) replacements for  
6 conventionally employed volatile amines and/or ammonia as  
7 neutralizers, and organic solvents as coalescents, respectively may  
8 be employed to substantially enhance the processability (pot life),  
9 mechanical and chemical resistance properties ( abrasion and stain  
10 resistance respectfully) as well as attain VOC reduction in wood  
11 coatings. A further benefit of the instant invention as applied to  
12 wood coatings is that unlike conventionally coalesced waterborne  
13 coatings, e.g. formulation D-1 latex formulations based upon the  
14 teachings of this invention, e.g. formulations D-2 through D-7, do  
15 not cause significant grain rise, thereby virtually eliminating the  
16 necessity for intercoat sanding. These data also demonstrate that  
17 subsets of the preferred combination of components herein disclosed  
18 (e.g. formulations D-3, D-5, and D-6) may provide considerable  
19 benefits relative to their conventional counterparts, such as  
20 Formulation No. 1; however, omission of one or more of the  
21 components of the combination herein disclosed leads to inferior  
22 results as compared to the inclusion of the full compliment.

23 Example #5

24 This example teaches the superiority of the present invention  
25 versus the prior art with respect to the productivity, VOC  
26 emissions, and performance quality in waterborne flexographic inks.

1 A latex flexographic ink formulation, was prepared by the  
 2 sequential dispersion of the indicated components (pigment  
 3 dispersion times and grind quality achievement was noted). The  
 4 resulting ink was applied via a #6 wire wound rod to bond paper,  
 5 and permitted to dry. Dry time (to touch) was measured under  
 6 conditions, of 72° F and 85% humidity. After 6 hours of drying @,  
 7 72° F and 85% humidity, heat seal resistance performance (face to  
 8 face) was measured at 25 psig. and 2 seconds contact time) the  
 9 results of this study are given in Table No. 5.

10 **Formulation:** in parts by weight; (in order of addition) E-2350  
 11 resin 267; neutralizer, as shown; surfactant, as shown; Defo 1020  
 12 defoamer 4.00 Ultra Inc.; coalescent<sup>a</sup>, as shown; calcium lithol  
 13 pigment 50% presscake, 400-Sun Chemical Corp.; Michemlube wax 5-  
 14 Michelman Inc., water, as required in order to produce a viscosity  
 15 of 27 seconds using a #2 Zahn cup. Relative dry ink color  
 16 intensities were measured by integrating thin film reflectance  
 17 spectra at 300-600 um wavelengths using a spectrophotometer after  
 18 48 hours of drying at the above conditions

19 Table No. 5

| 20 <u>Formulation</u> | <u>1</u>        | <u>2</u> | <u>3</u>            |
|-----------------------|-----------------|----------|---------------------|
| 21 neutralizer        | 28% ammonia aq, | 1D/2.00  | IH/1.40             |
| 22                    | 2.00            |          |                     |
| 23 surfactant         | Tamol 850/4.95  | 5A/1.80  | 5E/1.75             |
| 24 coalescent         | isopropanol/48  | 2A/10.5  | 2E/20.0             |
| 25                    | Texanol/24      | 3C/15.5  |                     |
| 26                    |                 | 4H/5.5   |                     |
| 27                    |                 |          |                     |
| 28 <u>Formulation</u> | <u>4</u>        | <u>5</u> | <u>6</u>            |
| 29 neutralizer        | 1F/2.00         | 1D/1.46  | 28% ammonia aq/2.00 |
| 30 surfactant         | 5K/1.55         | 5H/1.50  | Tamol 850/ 4.95     |
| 31 coalescent         | 3C/25.0         | 3C/18.0  | 3C/18.0             |
| 32                    |                 | 4H/7.0   | 4H/7.0              |

|    | <u>Formulation</u> | <u>VOC g/l<sup>5</sup></u> | <u>Dry to touch time</u><br><u>hr.</u> | <u>6 hr.Heat seal</u><br><u>resistance °C</u> | <u>Relative color</u><br><u>intensity.</u> |
|----|--------------------|----------------------------|--|---|--|
| 1  |                    |                            |  |   |  |
| 2  |                    |                            |  |   |  |
| 3  |                    |                            |  |   |  |
| 4  |                    |                            |  |   |  |
| 5  | 1                  | 144                        | 3.4                                    | 86  | 1.00                                       |
| 6  | 2                  | 4                          | 0.7                                    | 154   | 1.42                                       |
| 7  | 3                  | 3                          | 0.6                                    | 172   | 1.27                                       |
| 8  | 4                  | 5                          | 0.7                                    | 104   | 1.08                                       |
| 9  | 5                  | 4                          | 0.6                                    | 167   | 1.39                                       |
| 10 | 6                  | 7                          | 0.6                                    | 122   | 1.03                                       |

11  
12 Notes: The efficacy of the coalescent systems of the instant  
13 art in producing a faster drying, more strongly colored, and  
14 lower VOC acrylic latex based printing ink coating as compared to  
15 a conventionally coalesced counterpart are obvious from the  
16 preceding data, as are indications that incomplete application of  
17 the teachings of this disclosure may lead to inferior results.  
18 Note the deficiencies in the heat seal performance of formulation  
19 E-4 as compared to E-2, E-3, and E-5, the benefits of  
20 hyperdispersant use as indicated E-2 to E-5 vs. E-6.

#### 21 Example #6

22 This example teaches the utility of the instant  
23 invention in the production of superior waterborne anti-scuff  
24 overprint coatings for graphic arts applications.  
25 A 30% solution of water reducible styrene-acrylic copolymer resin  
26 in water was prepared by admixture of the indicated neutralizing  
27 agent-as shown, water, and Air Product Corp's Flexbond 28 resin.  
28 Thirty parts by weight (PBW) of the preceding solution, were  
29 admixed with 50 PBW of styrene- acrylic latex resin (Flexbond  
30 285, Air Products Corp.), coalescent, and surfactant(s) -as  
31 shown, poly ethylene wax, 2 PBW, and sufficient water to dilute  
32 the system to 100 PBW.

The resulting coating was applied, in line on a high speed six color lithographic cold web press, to a solid four color print pattern, followed by in line infrared drying, and folding.

Measurements of VOC (by EPA Method 24), offset, and blocking limited maximum allowable impression rates (impressions/ minute [IPM]), were made. The results are given in Table 6.

**Table 6**

| <u>Formulation</u> | <u>1</u>          | <u>2</u>                   | <u>3</u>     |
|--------------------|-------------------|----------------------------|--------------|
| neutralizer        | 28% ammonia/ 6.00 | AMP 95 <sup>1</sup> / 8.00 | AMP 95/ 8.00 |
| coalescent (s)     | isopropanol/ 12   | isopropanol/ 12            | 2G/ 4.50     |
| surfactant         | Tamol 850/ 2.05   | Tamol 850/ 2.05            | 5K/ 0.75     |
| <u>Formulation</u> | <u>4</u>          | <u>5</u>                   | <u>6</u>     |
| neutralizer        | 1G/ 6.00          | 1G/ 6.00                   | 1G/ 6.00     |
| coalescent (s)     | 2G/ 4.50          | 2G/ 4.50                   | 3C/ 3.65     |
| surfactant         | Tamol 850/ 2.05   | 5K/ 0.75                   | 4C/ 0.85     |
|                    |                   |                            | 2K/ 0.75     |
| <u>Performance</u> | <u>1</u>          | <u>2</u>                   | <u>3</u>     |
| VOC -g/l.          | 131               | 146                        | 27           |
| max IPM (offset)   | 8,240             | 9,235                      | 12,720       |
| max IPM (block)    | 10,150            | 9,950                      | 14,610       |
| <u>Performance</u> | <u>4</u>          | <u>5</u>                   | <u>6</u>     |
| VOC -g/l.          | 3                 | 4                          | 4            |
| max IPM (offset)   | 16,670            | 18,000 <sup>2</sup>        | 18,000       |
| max IPM (block)    | 17,130            | 18,000                     | 18,000       |

1 **Claims:**

2 What we claim is:

3 1) Compositions of matter comprising:

4 essentially nonvolatile reactive amines;

5 hydroxyl bearing, unsaturated esters and/or ethers and/or

6 ether-esters; and/or

7 combinations of non-hydroxyl bearing, unsaturated esters

8 and/or ethers and/or ether-esters, and/or saturated hydroxyl

9 bearing etherified and/or esterified oligomeric glycols

10 and/or oligools.

11 2) Compositions of matter comprising:

12 volatile amines and/or ammonia neutralizers;

13 hydroxyl bearing, unsaturated esters and/or ethers and/or

14 ether-esters; and/or

15 combinations of non-hydroxyl bearing, unsaturated esters

16 and/or ethers and/or ether-esters, and/or saturated hydroxyl

17 bearing etherified and/or esterified oligomeric glycols

18 and/or oligools.

19 3) Compositions of matter comprising:

20 essentially nonvolatile reactive amines; and

21 organic solvent coalescents.

22 4) Compositions of matter as defined in Claims 1, 2 and 3 having

23 as an additional component latex resin.

24 5) Compositions of matter as defined in Claims 1, 2, 3 and 4

25 having hypersurfactants as an additional component.

26 6) Compositions of matter as defined in Claim 5 in which the



1       hypersurfactants are derived from titanium or zirconium based  
2       organometalics.

3    7) Compositions of matter as in Claim 4 in which the latex resin  
4       is derived from poly vinyl acetate and/or acrylic and/or a  
5       copolymer thereof.

6

7

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WO 1999/032563 A3

(54) Title: LOW ENVIRONMENTAL TOXICITY LATEX COATINGS

(57) Abstract: Combinations of nonvolatile reactive amines, and hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters (and/or combinations of non-hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters, and saturated hydroxyl bearing etherified and/or esterified oligomeric glycols and/or oligools), as replacements for conventionally employed volatile amines and/or ammonia as neutralizers, and organic solvents as coalescents respectively, has been found to enable the production of economical, low to no VOC acrylic and vinyl copolymer latex based coatings, paints, and inks. Further enhancement may be had by substitution of hypersurfactants, in place of conventional soaps and/or dispersants and/or detergents, in combination with the aforementioned nonvolatile reactive amines, particularly as particulate dispersants in pigmented and/or reinforced coatings.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/24224

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : A01N 43/16

US CL : 514/451

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 514/451

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X          | US 4,343,884 A (MULLER et al.) 10 August 1982 (10.08.1982), see entire document.   | 1-7                   |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

04 April 2005 (04.04.2005)

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